

DECLARATION

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the attached document is a true English translation of Japanese
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[Title of the Invention]

Electrostatic Image Development
Toner, Process Cartridge, Fixing
Method, and Image Formation
Method

5 [Scope of Claims]

[Claim 1]

Electrostatic image development toner comprising at least a
binder resin, a charge control agent, and a colorant, characterized
in that the colorant is a black iron oxide compound containing a
10 10 to 45 weight % titanium component in terms of Ti atoms against
Fe atoms in a wavelength dispersive X-ray fluorescence spectrometry
method, Bragg angle 2θ peaks of the toner for a $\text{CuK}\alpha$ characteristic
X-ray appear at 32.9 ± 0.3 degrees (peak A) and 35.5 ± 0.3 degrees
(peak B), and an X-ray peak intensity ratio (A/B) for a scan speed
15 of 0.5 to 4 degrees/min. is in a range of 0.3 to 2.0.

[Claim 2]

The electrostatic image development toner according to claim 1,
characterized in that the colorant has a saturation magnetization
 σ_s of 0.5 to 30 emu/g.

20 [Claim 3]

The electrostatic image development toner according to claim
1 or 2, characterized in that an average primary particle diameter
of the black iron oxide compound is 0.05 to 2.0 μm .

[Claim 4]

25 The electrostatic image development toner according to any one
of claims 1 through 3, characterized in that the binder resin
includes two types of resin (A) and (B) which are different in
softening temperature, and the softening temperature (T_m) and glass
transition temperature (T_g) of the resin (A) and the resin (B)
30 satisfy following expressions:

$$T_m(A) > T_m(B)$$

$$|T_g(A) - T_g(B)| < 10 \text{ (}^\circ\text{C)}$$

$$30 \leq T_m(A) - T_m(B) \leq 60 \text{ (}^\circ\text{C)}$$

[Claim 5]

The electrostatic image development toner according to any one of claims 1 through 4, characterized in that the binder resin
5 includes a polyester resin.

[Claim 6]

The electrostatic image development toner according to any one of claims 1 through 5, characterized in that the charge control agent is a zirconium compound including zirconium and an aromatic
10 oxycarboxylic acid or an aromatic oxycarboxylic acid salt.

[Claim 7]

A toner image fixing method characterized by using a fixing device for thermally fixing a toner image by causing a support member supporting the toner image to pass through a clearance between two
15 rollers, wherein the fixing roller contacting a toner image supporting surface has a thickness of equal to or less than 1.0 mm and an applied pressure in the clearance between the two rollers (roller load/contact area) is equal to or less than 1.5×10^5 Pa, and fixing a toner image produced by using the electrostatic image
20 development toner according to any one of claims 1 through 6.

[Claim 8]

A process cartridge which integrally supports a photoconductor and at least any one of a charge means, a development means, and a cleaning means and may be attached to and detached from an image
25 forming apparatus, characterized by comprising at least a development means including the electrostatic image development toner according to any one of claims 1 through 6.

[Claim 9]

An image formation method characterized by using the
30 electrostatic image development toner according to any one of claims 1 through 6 in an image forming apparatus including at least a charge device for performing a charge by causing a photoconductor and a charge member to contact and applying voltage to the charge member.

[Name of Document] Specification

[0001]

[Technical Field]

5 The present invention relates to electrostatic image development toner for use in electrophotography etc., a process cartridge including the toner, a method for fixing a toner image produced by using the toner, and an image formation method using the toner.

[0002]

[Background Art]

10 Conventionally, there are electrophotography methods such as described in United States Patent No. 2297691, Japanese Patent Publication No. Sho. 49-23910, and Japanese Patent Publication No. Sho. 43-24748. A common method is to form an electric latent image on a photoconductor through procedures by using a photoconductive
15 substance, develop the latent image with dry toner, transfer a toner image onto a sheet etc., and fix the image with heat or pressure so as to obtain a copy.

[0003]

20 Methods for developing the electric latent image may be divided into liquid development methods using a developer with pigments and dyes finely dispersed in an insulating organic liquid, and dry development methods including a cascade method, a magnetic brush method, a powder cloud method, etc. using toner with a colorant such as carbon black dispersed in a natural or synthesized resin.
25 The dry development methods include one-component development methods and two-component development methods using a carrier.

[0004]

30 Methods for thermally fixing a toner image onto a transfer sheet may be divided into contact fixing methods and non-contact fixing methods. The contact fixing methods include a heat roller fixing method and a belt fixing method. The non-contact fixing methods include a flash fixing method and an oven (atmosphere) fixing method.

The heat roller fixing method is a fixing method with extremely high heat efficiency because the toner image directly contacts a heat roller, and is contributive to size reduction of an apparatus. Therefore, the heat roller fixing method is widely used as a common method.

[0005]

In recent years, energy conservation is promoted more than ever so that some apparatuses disconnect a heat source during a waiting time in which the fixing is not performed. Such apparatuses require immediately heating up the heat roller to desired temperature in an extremely short time when the heat source is connected.

Attempts are made to form a fixing roller contacting a toner supporting surface with a thickness of equal to or less than 1.0 mm for improving the heat efficiency of a fixing device used in the apparatus (Japanese Patent Application Laid-Open No. 2002-82474 and Japanese Patent Application Laid-Open No. Hei09-222750 ... Patent documents 1 and 2). Thereby, it becomes possible to heat up to desired temperature in an extremely short time.

[0006]

However, the fixing roller with a thickness of equal to or less than 1.0 mm is not mechanically strong. A large load may not be applied to the fixing roller because the roller may be deformed when a clearance between the rollers undergoes application of the large load.

Therefore, the toner to be used in the fixing device requires low temperature fixability incomparably better than conventional toner.

[0007]

Some technical approaches are conventionally made for solving the problem.

For example, Japanese Patent No. 2743476 discloses a roll fixing toner including resin coated core particles made of a polyester

resin and a wax with a polar radical and specifying melting viscosities of the polyester resin and the wax, Japanese Patent Application Laid-Open No. Hei3-122661, Japanese Patent Application Laid-Open No. Hei4-85550, and Japanese Patent Publication No. Hei8-16804 disclose a film fixing toner including a particular polyester resin and a particular release agent and specifying a melting viscosity of the polyester resin at 80 to 120 °C, a gradient of a melting viscosity temperature graph of the polyester resin, and a melting viscosity of the particular release agent, Japanese Patent Publication No. Hei8-12459 discloses a film fixing capsule toner including a particular polyester resin and a particular release agent and specifying a melting viscosity of the polyester resin at 80 to 120 °C, a gradient of a melting viscosity temperature graph of the polyester resin, and a melting viscosity of the particular release agent, Japanese Patent Publication No. Hei7-82250 discloses a film fixing toner including a particular polyester resin, a particular organometallic compound, and a particular release agent and specifying a melting viscosity of the polyester resin at 120 to 150 °C, a gradient of a melting viscosity temperature graph of the polyester resin, and a melting viscosity of the particular release agent, Japanese Patent Publication No. Hei7-72809 discloses toner including a styrene-acryl resin and specifying a relation between melting viscosity and temperature measured at 110 to 130 °C, and Japanese Patent Application Laid-Open No. Hei10-246989 discloses toner including a particular charge control agent and specifying an average viscosity gradient.

[0008]

In addition, improvement in image quality is recently promoted more than ever so that a toner particle diameter becomes smaller and smaller. It is known that toner of a small particle diameter has deteriorated fixability because the toner particles, undergoing pressure application between the fixing rollers, difficultly receive the pressure. Such a tendency is especially significant

in a case of use in the fixing device with a low contact pressure.
[0009]

Further, attempts are recently made to use a black metal compound fine powder with high safety and excellent heat conductivity in place of carbon black.

For example, Japanese Patent No. 2736680 (Patent document 3) discloses a mixture of Fe_2TiO_5 and Fe_2O_3 - FeTiO_3 solid solutions with an average particle diameter of 0.1 to 0.5 μm , Japanese Patent No. 3101782, Japanese Patent No. 3108823, and Japanese Patent No. 3174960 disclose a magnetic iron oxide containing 25 to 30 % FeO , Japanese Patent No. 3224774 and Japanese Patent No. 3261088 disclose a magnetite with a residual magnetization of equal to or less than 6 emu/g, Japanese Patent Application Laid-Open No. 2000-319021 discloses an iron oxide particle with Ti inside and Ti and Fe outside, Japanese Patent Application Laid-Open No. 2002-129063 (Patent document 4) discloses a rutile TiO_2 mixed phase crystal having a saturation magnetization of 0.5 to 10 emu/g and a particle diameter of 0.1 to 0.4 μm with a coating of Fe_2TiO_4 , Japanese Patent Application Laid-Open No. 2002-189313 (Patent document 5) discloses a metal compound having a saturation magnetization of equal to or less than 30 emu/g and a dielectric loss of equal to or less than 50, Japanese Patent Application Laid-Open No. 2002-196528 (Patent document 6) discloses a metal compound having a saturation magnetization of equal to or less than 40 emu/g to be contained by an amount of equal to or less than 20 parts by weight, and Japanese Patent Application Laid-Open No. 2000-10344 (Patent document 7) discloses a powder of black hematite fine particles and black hydrous iron oxide fine particles.

[0010]

In case the toner of conventional art is used in the fixing device with a thin-walled roller and a low contact pressure under circumstances the energy conservation is increasingly promoted, it is impossible to achieve sufficient fixability.

[Means for Solving the Problems]

The present invention may provide means (1) through (9) as follows.

(1) Electrostatic image development toner including at least a binder resin, a charge control agent, and a colorant, characterized in that the colorant is a black iron oxide compound containing a 10 to 45 weight % titanium component in terms of Ti atoms against Fe atoms in a wavelength dispersive X-ray fluorescence spectrometry method, Bragg angle 2θ peaks of the toner for a $\text{CuK}\alpha$ characteristic X-ray appear at 32.9 ± 0.3 degrees (peak A) and 35.5 ± 0.3 degrees (peak B), and an X-ray peak intensity ratio (A/B) for a scan speed of 0.5 to 4 degrees/min. is in a range of 0.3 to 2.0.

(2) The electrostatic image development toner as described in (1), characterized in that the colorant has a saturation magnetization σ_s of 0.5 to 30 emu/g.

(3) The electrostatic image development toner as described in (1) or (2), characterized in that an average primary particle diameter of the black iron oxide compound is 0.05 to 2.0 μm .

(4) The electrostatic image development toner as described in any one of (1) through (3), characterized in that the binder resin includes two types of resin (A) and (B) which are different in softening temperature, and the softening temperature (T_m) and glass transition temperature (T_g) of the resin (A) and the resin (B) satisfy following expressions:

$$T_m(A) > T_m(B)$$

$$|T_g(A) - T_g(B)| < 10 \text{ (}^\circ\text{C)}$$

$$30 \leq T_m(A) - T_m(B) \leq 60 \text{ (}^\circ\text{C)}$$

(5) The electrostatic image development toner as described in any one of (1) through (4), characterized in that the binder resin includes a polyester resin.

(6) The electrostatic image development toner as described in any one of (1) through (5), characterized in that the charge control

agent is a zirconium compound including zirconium and an aromatic oxycarboxylic acid or an aromatic oxycarboxylic acid salt.

(7) A toner image fixing method characterized by using a fixing device for thermally fixing a toner image by causing a support member supporting the toner image to pass through a clearance between two rollers, wherein the fixing roller contacting a toner image supporting surface has a thickness of equal to or less than 1.0 mm and an applied pressure in the clearance between the two rollers (roller load/contact area) is equal to or less than 1.5×10^5 Pa, and fixing a toner image produced by using the electrostatic image development toner as described in any one of (1) through (6).

(8) A process cartridge which integrally support a photoconductor and at least any one of a charge means, a development means, and a cleaning means, and may be attached to and detached from an image forming apparatus, characterized by including at least a development means including the electrostatic image development toner as described in any one of (1) through (6).

(9) An image formation method characterized by applying the electrostatic image development toner as described in any one of (1) through (6) to an image forming apparatus including at least a charge device for performing a charge by causing a photoconductor and a charge member to contact and applying voltage to the charge member.

[0014]

[Best Mode for Carrying out the Invention]

In a colorant of electrostatic image development toner according to the present invention, a new black oxide compound as an alternative to carbon black has a structure of polycrystalline particle powder including an Fe_2O_3 - FeTiO_3 solid solution. As the polycrystalline particle powder, a black oxide compound containing a 10 to 45 weight percent titanium component in terms of Ti atoms against Fe atoms in a wavelength dispersive fluorescence spectrometry method, and showing Bragg angle 2θ peaks for a CuK

α characteristic X-ray at 32.9 ± 0.3 degrees (peak A) and 35.5 ± 0.3 degrees (peak B) with a ratio of X-ray intensity peaks (A/B) in a range of 0.3 to 2.0 for a scan speed of 0.5 to 4 degrees/min. is extremely adequate for the alternative to the carbon black owing to low magnetism, high blackness, and excellence in dispersibility and charge capability.

[0015]

The peaks reflect a crystalline structure of Fe_2O_3 . It is important that the peak A/B ratio is in the range of 0.3 to 2.0, and crystal faces evenly growing are favorable. The structure with the ratio of more than 2.0 causes strong cohesion between particles and bad dispersibility of toner so that fixing is defectively performed due to insufficient heat conductivity of the toner. The structure with the ratio of less than 0.3 causes low volume resistivity so that a charge amount may not be sufficiently obtained and/or a built-up rate of the charge is insufficient. With the peak A/B ratio in the range of 0.3 to 2.0, fixing of the toner may be favorably performed at low temperature, and the charge amount and the charge built-up rate of the toner become adequate.

[0016]

The black iron oxide compound having the specific X-ray diffraction intensity may be produced by performing grinding after thermal calcinations of 700 to 1000 °C, and preferably, 800 to 1000 °C in a non-oxidative atmosphere on powder of magnetite particles coated with a titanium compound, mixed powder of magnetite particle powder with a titanium compound, or reduction powder obtained by reducing powder of hematite particles coated with a titanium compound. The new black iron oxide compound having the X-ray diffraction intensity according to the present invention is obtained by controlling cooling temperature after the calcinations. In case of performing slow cooling by equal to or less than 400 °C /hr after the calcinations, the coating of the titanium compound and the crystal faces may become uneven. In case of performing rapid

cooling by equal to or more than 1500 °C/hr after the calcinations, the coating of the titanium compound may be easily detached. Consequently, the desired X-ray diffraction intensity may not be achieved in either of the cases. Preferably, the magnetite particle powder coated with the titanium compound may be used as a material because non-magnetic particles with a small magnetization value may be obtained.

[0017]

The polycrystalline particle powder including the $\text{Fe}_2\text{O}_3\text{-FeTiO}_3$ solid solution is a favorable structure of the black oxide compound according to the present invention in view of the blackness and the low magnetism.

Particles of the magnetite particle powder and the hematite particle powder may be formed in any shapes including grain shapes, globular shapes, acicular shapes, etc. The particle to be used may have a largeness of 0.03 to 1.5 μm .

[0018]

There is a correlation between a size of the material particle and a size of a product particle. The product of a small particle diameter may be made from the material of a small particle diameter, and the product of a large particle diameter may be made from the material of a large particle diameter.

[0019]

Either of a hydrated oxide, a hydroxide, or an oxide of titanium may be used as the titanium compound. A water-soluble titanium compound is preferable in case of mixing with the magnetite particle powder. An amount of the titanium compound to be contained may be 10 to 45 weight percent in terms of Ti atoms against Fe atoms. In case the weight percent is less than 10, the magnetization value of the produced black pigment particle powder become large so that development performance of toner is deteriorated and density of image decreases. In case the weight percent is more than 45, a large amount of TiO_2 is produced so that an L value (lightness) increases

and coloring performance of toner is deteriorated although the produced black pigment particle powder is non-magnetic.

[0020]

In the present invention, a ratio of the titanium component in the black oxide compound is measured as a ratio of Ti atoms to Fe atoms by the wavelength dispersive X-ray fluorescence spectrometry method. Measurement is performed by using a wavelength dispersive X-ray fluorescence spectrometer so that the ratio may be determined from an obtained ratio of main peaks.

10 [0021]

In the electrostatic image development toner according to the present invention, the black iron oxide compound is contained normally by 5 to 45 parts by weight, and preferably, by 10 to 30 parts by weight of a binder resin.

15 In case the ratio is less than 5 parts by weight, coloring performance of the toner is insufficient so that the toner takes on redness, and moreover fixing temperature may not be sufficiently reduced. In case the ratio is more than 45 parts by weight, development performance decreases because an specific gravity of the toner becomes excessive.

20

[0022]

According to the present invention, a favorable saturation magnetization σ_s of a colorant may be 0.5 to 30 emu/g.

In case the saturation magnetization of the colorant is more than 30 emu/g, holding power between the toner and a toner carrier including a magnet such as a magnetic sleeve and a magnetic brush becomes intense so that development on a photoconductor may not be adequately performed. In case the saturation magnetization of the colorant is less than 0.5 emu/g, the holding power becomes low so that toner scattering and scumming occur in a deteriorated manner.

25
30

Measurement of the saturation magnetization of the colorant is performed by using a magnetization measurement device BHU-60

manufactured by Riken Denshi Co., Ltd. The saturation magnetization is determined from a hysteresis loop obtained by applying a magnetic field swept to 10 kOe to the colorant filled in a cell with an inner diameter of 7 mm and a height of 10 mm.

5 [0023]

According to the present invention, an average primary particle diameter of the black iron oxide compound in the toner may be 0.05 to 2.0 μm , and preferably, 0.1 to 0.5 μm in view of dispersibility in the toner.

10 The average primary particle diameter of the black iron oxide compound is an average of values obtained by measurement of an electron micrograph by a Hitachi transmission electron microscope H-9000.

[0024]

15 If necessary, the material particles may be coated with a known sintering inhibitor before the thermal calcinations in the above-mentioned method. By the coating, sintering of individual particles and sintering of a set of particles during the thermal calcinations may be prevented so that black pigment particle powder
20 with excellent dispersibility may be obtained. A compound containing one or more elements including Al, Ti, Si, Zr, and P may be used as a sintering inhibitor not impairing the desired properties of the black pigment particle powder of the present invention. The sintering inhibitor is normally contained by 0.1
25 to 15.0 atom percent of Fe and Ti atoms. The ratio may be preferably more than 0.1 atom percent for achieving an adequate sintering prevention effect. In case the ration is more than 15.0 atom percent, magnetite appears in the produced black pigment particle powder so that the non-magnetic black iron oxide compound may not be easily
30 obtained.

[0025]

For further increasing the blackness, it is preferable to fix a black dye/pigment or a blue dye/pigment on the surface of the

black pigment particle by using a Mechanomil (manufactured by Osaka Seiko Co., Ltd.) or a Mechanofusion System (manufactured by Hosokawa Micron Corporation).

The black dyes/pigments include iron black, aniline black, graphite, fullerene, etc. The blue dyes/pigments include cobalt blue, alkali blue, victorian blue lake, phthalocyanine blue, metal-free phthalocyanine blue, partially chlorinated phthalocyanine blue, fast sky blue, indanthrene blue BC, etc. However, any other dyes and pigments may also be used.

10 [0026]

Two types of resin being different in softening temperature, a resin (A) and a resin (B) may be characteristically used as the binder resin according to the present invention. The softening temperature (T_m) as well as glass transition temperature (T_g) of the resin (A) and the resin (B) may satisfy following expressions so that further energy conservation may be achieved.

$$T_m(A) > T_m(B)$$

$$|T_g(A) - T_g(B)| < 10 \text{ (}^\circ\text{C)}$$

$$30 \leq T_m(A) - T_m(B) \leq 60 \text{ (}^\circ\text{C)}$$

20 [0027]

In case two types of toner being different in softening temperature are used in a conventional toner including carbon black, softness of the resin and high compatibility of polymer deteriorate productivity due to cracking resistance of the resin, and in addition, storage stability against heat is insufficient. However, the toner including the black iron oxide compound according to the present invention achieves favorable grinding owing to an occurrence of a cracking interface between the toner and the resin. In addition, the black iron oxide compound has higher heat conductivity than the carbon black so that the fixing may be favorably performed. Further, the black iron oxide compound with the X-ray diffraction intensity within the specific range according to the present invention achieves excellent dispersibility of the

toner so that a filler effect may be produced. Thereby, hardness of the toner increases so that storage stability against heat as well as hot offset resistance may be improved. Furthermore, the black iron oxide compound may increase dispersibility of the resin or dispersibility between resin and other materials such as a mold release agent by giving hazardous effects to the resin in a kneading process. Consequently, improvement in reducing fogging may be achieved owing to the excellent dispersibility.

[0028]

An absolute value of $T_g(A) - T_g(B)$ is preferably less than 10 °C. In case the value is equal to or larger than 10 °C, compatibility decreases in the kneading process so that both low temperature fixability and hot offset resistance may hardly become sufficient. A further preferable value is equal to or less than 7 °C.

In addition, by setting $T_m(A) - T_m(B)$ at 30 to 60 °C, both the low temperature fixability and the hot offset resistance may be nicely achieved so that a sufficient fixing temperature range may be retained. A further preferable value is 35 to 55 °C. Further low temperature fixability may be obtained if the resin is a polyester resin.

[0029]

The softening temperature (T_m) of the binder resin is measured with a Capillary Rheometer Shimadzu Flowmeter (manufactured by Shimadzu Corporation) in conformity with a method as described in JIS K72101. Specifically, a sample of 1 cm cube is pushed out of a nozzle having a diameter of 1 mm and a length of 1 mm by applying a load of 20 Kg/cm² with a plunger while heating is performed at a rising temperature rate of 6 °C/min. so that a plunger descent amount-temperature curve is obtained. When h represents a height of an obtained sigmoid curve, the softening temperature (T_m) is determined as temperature corresponding to $h/2$ (temperature at which a half of the resin flows out).

[0031]

The glass transition temperature (T_g) of the binder resin is measured with a differential scanning calorimeter manufactured by Shimadzu Corporation, DSC-60. After performing heating up to 200 °C from room temperature at a rising temperature rate of 10 °C/min., and subsequently cooling down to room temperature at a falling temperature rate of 10 °C/min., measurement is performed at a rising temperature rate of 10 °C/min. The glass transition temperature (T_g) is determined as a point of a curve corresponding to $h/2$ when h represents a height between baselines before and after the glass transition.

Preferably, the toner may have a volume average particle diameter of from 4 to 7.5 μm , and particles with a size equal to or less than 5 μm may have a particle diameter distribution of 60 to 80 percent by number for achieving good reproducibility of thin lines.

In case the volume average particle diameter is less than 4 μm , transfer efficiency and blade cleaning efficiency are likely to decrease.

In case the volume average particle diameter is more than 7.5 μm , it is difficult to prevent the toner from scattering beyond letters and lines.

Additionally, in case the particle diameter distribution of particles of a size equal to or less than 5 μm is less than 60 percent by number, reproducibility of thin lines is deteriorated.

In case the particle diameter distribution of particles of a size equal to or less than 5 μm is more than 80 percent by number, adhesion to a development sleeve may occur in an aggravated manner because a fine powder amount becomes excessive.

[0032]

The toner according to the present invention includes a charge control agent for controlling polarity. For example, nigrosine dyes, quaternary ammonium salts, amino group-containing polymers, metal-containing azo dyes, complex compounds of salicylic acid, phenol compounds, etc. may be used as the charge control agent.

In particular, zirconium compounds including zirconium and an aromatic oxycarboxylic acid or a salt thereof are preferable not only because the zirconium compounds including zirconium and an aromatic oxycarboxylic acid or a salt thereof may provide a large amount of charge and a good rate of charge built-up, but also because the zirconium and the black iron oxide compound according to the present invention may have an interaction parallel to metal crosslinking to cause a filler effect so that storage stability against heat of the toner may be improved.

10 [0033]

Any of known conventional resins may be used as the binder resin used in the toner of the present invention. For example, styrene resins (homopolymers or copolymers containing styrene or styrene substituent) such as polystyrene, poly- α -stilstyrene, styrene-chlorostyrene copolymer, styrene-propylene copolymer, styrene-butadiene copolymer, styrene-vinyl chloride copolymer, styrene-vinyl acetate copolymer, styrene-maleic acid copolymer, styrene acrylic acid ester copolymer, styrene-methacrylic acid ester copolymer, styrene- α -methyl chloroacrylate copolymer, and styrene-acrylonitrile-acrylate copolymer, polyester resin, epoxy resin, vinyl chloride resin, rosin-modified maleic resin, phenol resin, polyethylene resin, polypropylene resin, petroleum resin, polyurethane resin, ketone resin, ethylene-ethylacrylate copolymer, xylene resin, and polyvinyl butylate resin. In particular, the polyester resin may be preferably used for improving fixing properties.

[0034]

The polyester resin is obtained from condensation polymerization of an alcohol ingredient and a carboxylic acid ingredient. The alcohol ingredient to be used may be glycols such as ethylene glycol, diethylene glycol, triethylene glycol, and propylene glycol, etherated bisphenols such as 1,4-bis (hydroxymeta) cyclohexane and

bisphenol A, divalent alcohol monomers, and polyvalent alcohol monomers with a valence of three or higher, for example. The carboxylic acid ingredient may be divalent organic acid monomers such as maleic acid, fumaric acid, phthalic acid, isophthalic acid, 5 terephthalic acid, succinic acid, and malonic acid, polyvalent carboxylic acid monomers with a valence of three or higher such as 1,2,4-benzene tricarboxylic acid, 1,2,5- benzene tricarboxylic acid, 1,2,4-cyclohexane tricarboxylic acid, 1,2,4-naphthalene tricarboxylic acid, 1,2,5-hexane tricarboxylic acid, 1,3- 10 dicarboxyl-2-methylene carboxypropane, and 1,2,7,8-octane tetracarboxylic acid, for example.

Preferably, the glass transition temperature (T_g) of the polyester resin may be 58 to 75 °C.

[0035]

15 The above resins may be used alone or in combination.

Additionally, a method for manufacturing the resin is not limited so that any method including block polymerization, solution polymerization, emulsion polymerization, and suspension polymerization may be applied.

20 [0036]

According to the present invention, the toner may include a wax component for improving releasability at a time of fixing. For example, a polyolefin wax such as polypropylene wax and polyethylene wax and a natural wax such as candelilla wax, rice wax, and carnauba 25 wax may be used.

An additive amount of the wax component is preferably 0.5 to 10 parts per hundred parts by weight of the binder resin.

[0037]

The toner may include another additive if necessary. The additive 30 may be silica, aluminum oxides, or titanium oxides, for example. If fluidity improvement is primarily intended, the additive may

be appropriately selected among hydrophobically modified silica and rutile fine particle titanium oxide having an average primary particle diameter of 0.001 to 1 μm , and preferably 0.005 to 0.1 μm . In particular, organosilane surface treatment silica or titania are preferable. The additive may be used normally at 0.1 to 5 weight percent, and preferably 0.2 to 2 weight percent.

[0038]

The toner according to the present invention may be employed as a one-component dry toner, or a two-component dry toner blended with a carrier.

The carrier to be blended in the two-component dry toner including the toner according to the present invention may be a powder with a particle diameter of 30 to 1000 μm containing glass, iron, ferrite, nickel, zirconium, or silica as a main component, or alternatively, a powder of such particles with a coating of styrene-acryl resins, silicone resins, polyamide resins, or polyvinylidene fluoride resins.

[0039]

(Method for manufacturing the toner)

A toner manufacturing method including a process of mechanically mixing toner ingredients containing at least the binder resin, the main charge control agent, and the black iron oxide compound, a melt kneading process, a pulverization process, and a classification process may be used as a method for manufacturing the toner according to the present invention. A method in which a powder occurring in the pulverization process and the classification process except for particles to be a finished product may be reused in the mechanical mixing process and the melt kneading process is also applicable.

The "powder occurring in the pulverization process and the classification process except for particles to be a finished

product" (by-product) represents fine particles or coarse particles of a diameter not within a size desired for the finished product occurring in the pulverization process after the melt kneading process, or such particles occurring in the classification process.

5 When the by-product is added in the mixing process or the melt kneading process, a weight proportion of the by-product to other materials may be preferably from 1-99 to 50-50.

[0040]

10 The mixing process of mechanically mixing toner ingredients including at least the binder resin, the main charge control agent, and the black iron oxide compound may be performed by using a normal mixing machine with a rotating impeller under a normal condition without limitations.

[0041]

15 After the mixing process is completed, the mixed material is put in a kneading machine to undergo the melt kneading. A continuous kneading machine with one or two axis, or a batch kneading machine with a roll mill may be used as the melt kneading machine.

It is important to performing the melt kneading under an appropriate condition so that molecular chain rupture of the binder resin may not arise. Specifically, melt kneading temperature may be set based on the softening temperature of the binder resin because temperature excessively lower than the softening temperature causes a gross occurrence of the rupture while excessively high temperature
20 inhibits dispersion.
25

[0042]

After the melt kneading process is completed, the kneaded material is pulverized. In the pulverization process, coarse pulverization is firstly performed so that fine pulverization is
30 secondly performed. Preferably, the pulverization may be performed by crushing the kneaded mixture against a collision board in a jet

stream or using a narrow clearance between a mechanically rotating rotor and a stator.

[0043]

After the pulverization process is completed, the pulverized
5 material is classified in an airflow through centrifugal force so that the toner of a predetermined particle diameter, for example, an average diameter of 5 to 20 μm may be produced.

In preparing a developer, the produced toner may be additionally mixed with inorganic fine particles such as the hydrophobic silica
10 fine powder for improving fluidity, storage stability, developability, and transfer quality of the toner.

The mixing of an external additive is performed with a normal powder mixing machine. In such cases, the mixing machine may be equipped with a jacket etc. for adjusting inner temperature. For
15 modifying history of loading on the external additive, the addition may be intermittently or gradually performed. Alternatively, a rotation number or rotation speed of the mixing machine, time, or temperature may be changed. The loading may be performed intensely at first and then weakly, or vice versa.

20 A mixing facility such as a V-blender, a rocking mixer, a Loedige mixer, a nauta mixer, and a Henschel mixer may be employed.

[0044]

A measurement method is described as follows.

The measurement by the wavelength dispersive X-ray fluorescence
25 spectrometry according to the present invention is performed by using a wavelength dispersive X-ray fluorescence spectrometer. Fluorescence X-ray conditions are as follows.

Voltage: 50 kv, current: 50 mA, Rh tube, under vacuum

The X-ray diffraction measurement according to the present
30 invention may be performed with $\text{CuK}\alpha$ radiation by using an RINT1100 manufactured by Hitachi, Ltd. under following conditions.

X-ray tube: Cu, tube voltage: 50 KV, tube current: 30 Ma, scan speed:
2 degrees/min.

[0045]

Fig. 1 illustrates an example of a fixing device to be used in
5 the present invention. A numeral 1 designates a fixing roller and
a numeral 2 designates a pressure roller. The fixing roller 1
includes a metal cylinder 3 made of a heat conductive material such
as aluminum, iron, stainless or brass. The metal cylinder 3 is
covered with an offset prevention layer 4 of RTV (a generic name
10 for room temperature vulcanizing rubbers), silicone rubber,
tetrafluoroethylene-perfluoroalkylvinylether (PFA),
polytetrafluoroethylene (PTFE), or the like. A heat lamp 5 is
disposed in the fixing roller 1. A metal cylinder 6 of the pressure
roller 2 may be generally made from the material used for the metal
15 cylinder 3 of the fixing roller 1. The metal cylinder 6 is covered
with a offset prevention layer 7 of PFA, PTFA, or the like. A heat
lamp 8 is optionally disposed in the pressure roller 2.

[0046]

The fixing roller and the pressure roller rotate while contacting
20 under pressure from springs on both sides (not shown).

Fixing is performed by passing an attachment support member S
(transfer sheet such as paper) of a toner image T through a clearance
between the fixing roller 1 and the pressure roller 2.

The metal cylinder of the fixing roller has a thickness of equal
25 to or less than 1.0 mm in the fixing device according to the present
invention. Thereby, a temperature build-up property of the fixing
roller may be improved so that temperature may be raised to a desired
level in a very short time.

A preferable thickness of the metal cylinder may be 0.2 to 0.7
30 mm, though varying according to strength and heat conductivity of
the used materials.

[0047]

The applied load at the clearance between the fixing roller and the pressure roller (pressure) is preferably equal to or less than 1.5×10^5 Pa. The pressure is a value determined by dividing a load applied to the ends of the rollers by a roller contact area.

The roller contact area may be obtained by entering a sheet having a property of significantly changing a surface character when heated, such as an OHP sheet, through the clearance between the rollers heated to fixing capability temperature, holding the sheet for several tens of seconds, and ejecting the sheet so that an area of a portion changing the surface character is measured.

Higher pressure is better for fixing the toner image. However, in the fixing device with the fixing roller including the metal cylinder of 1.0 mm or less thickness, a large load may not be applied because the roller may be distorted. The load may be equal to or less than 1.5×10^5 Pa, and preferably 0.5×10^5 to 1.0×10^5 Pa.

[0048]

Fig. 2 schematically illustrates a structure of an image forming apparatus including a process cartridge provided with the electrostatic image development toner according to the present invention. In Fig. 2, a numeral 1 designates an overall process cartridge, a numeral 2 designates a photoconductor, a numeral 3 designates a charge means, a numeral 4 designates a development means, and a numeral 5 designates a cleaning means.

According to the present invention, at least the development means 4 and one or more of other components including the photoconductor 2, the charge means 3, the cleaning means 5 may be integral with the process cartridge, which is attachable to and detachable from an image forming apparatus such as a copier, a printer, etc.

[0049]

The photoconductor of the image forming apparatus used in the present invention is driven to rotate at a predetermined circumferential velocity. In a rotation process, the photoconductor
5 undergoes uniform application of positive and negative charge at a predetermined potential on a circumferential surface, and subsequently image exposure by an image exposure means such as a slit exposure or a laser beam scanning exposure. Thereby, an electrostatic latent image is formed on the circumferential surface
10 of the photoconductor. Then the development means develops the formed electrostatic latent image to be a toner image. The transfer means transfers the developed toner image onto a transfer material fed to a clearance between the photoconductor and the transfer means from a sheet feed part in synchronization with the rotation of the
15 photoconductor. The transfer material onto which the image is transferred is separated from the photoconductor surface, delivered to an image fixing means, which performs image fixing, and ejected out of the apparatus as a duplication (copy). The cleaning means cleans transfer residual toner from the surface of the
20 photoconductor after the image transfer. The photoconductor is reused for image formation after undergoing charge removal.

[0050]

In the image forming apparatus, the image fixing means is preferably the fixing device with the fixing roller of the specified
25 thickness (equal to or less than 1.0 mm) and the specified pressure between the fixing roller and the pressure roller (equal to or less than 1.5×10^5 Pa).

In addition, the charge means is preferably a charge device which performs charging by bringing a charge material into contact with
30 a photoconductor and applying voltage to the charge material. The voltage may be uniformly applied to the developer by using such

a charge device as a charge means so that an image without fogging may be achieved.

[0051]

[Embodiment]

5 Following is a specific description of the present invention through an embodiment. However, the present invention may not be limited to the description.

[0052]

(Examples of producing the black iron oxide compound)

10 (1) Examples of producing black iron oxide compounds 1 through 4: Calcination is performed on magnetite particle powder of magnetite particles coated with titanium hydroxide in nitrogen atmosphere at calcination temperature and during a calcination time as described in Table 1. After cooling, pulverization is performed
15 on the calcined powder in a ball mill. Thereby, the black iron oxide compound is obtained.

 (2) Examples of producing black iron oxide compounds 5 through 8: Calcination is performed on mixed powder of hematite particle powder with titanium oxide in nitrogen atmosphere at calcination
20 temperature and during a calcination time as described in Table 1. After cooling, pulverization is performed on the calcined powder in a ball mill. Thereby, the black iron oxide compound is obtained.

 (3) Examples of producing black iron oxide compounds 9 through 4: Calcination is performed on reduction powder obtained by reducing
25 powder of hematite particles coated with titanium hydroxide in nitrogen atmosphere at calcination temperature and during a calcination time as described in Table 1. After cooling, pulverization is performed on the calcined powder in a ball mill. Subsequently, a blue dye/pigment (metal free phthalocyanine blue)
30 is fixed on the surface of the black pigment particles at 600 °C by using a Mechanofusion System manufactured by Hosokawa Micron

Corporation.

[0053]

Table 1 provides manufacturing conditions and properties of each black iron oxide compound.

	Ti compound coating amount (Ti atoms weight percent of Fe atoms)	Calcination temperature (°C)	Calcination time (min.)	Cooling rate (°C/hr)	Average primary particle diameter (µm)
Black iron oxide compound 1	10	800	120	400	0.02
Black iron oxide compound 2	10	1000	100	1500	2.2
Black iron oxide compound 3	45	900	120	450	2.5
Black iron oxide compound 4	45	700	120	600	0.04
Black iron oxide compound 5	35	850	110	1200	0.05
Black iron oxide compound 6	20	950	100	1400	2.0
Black iron oxide compound 7	12	820	110	1000	1.5
Black iron oxide compound 8	28	760	120	900	0.2
Black iron oxide compound 9	16	880	120	800	0.9
Black iron oxide compound 10	6	900	100	600	1.5
Black iron oxide compound 11	52	860	120	1200	0.08
Black iron oxide compound 12	30	950	120	350	1.1
Black iron oxide compound 13	22	800	120	1550	1.9

5 [0054]

Embodiment 1

(Toner Formula)

Styrene-n-butylacrylate copolymer

(T_m 155 °C, T_g 63 °C)

70 parts by weight

10 Black iron oxide compound 1

25 parts by weight

Carnauba wax

4 parts by weight

Charge control agent (chrome azo dye) 1 part by weight

The materials as described in the formula are kneaded, pulverized, and classified by using a twin screw extruder so that particles of 5 μ m weight average particle diameter are formed. Then silica fine powder (R-972, manufactured by Client Japan) of 0.5 parts by weight is mixed in with a Henschel mixer so as to obtain toner.

The toner is mixed with carrier of ferrite particles of 50 μ m average particle diameter coated with silicone resin at a toner concentration of 4.0 weight percent to produce a developer.

10 [0055]

① Method for evaluating fixing performance

A fixing device of a configuration as shown in Fig. 1 (pressure: 0.7×10^5 Pa. S) is mounted on an IMAGIO MF655 manufactured by Ricoh Co., Ltd. Copying is performed under changing temperature so that a fixed image is obtained.

The fixed image is taped up with mending tape (manufactured by 3M). The tape is slowly peeled off after application of constant pressure. Before and after image densities are measured with a Macbeth densitometer and a fixing ratio is calculated by evaluating a following expression. The temperature of the fixing roller is reduced in a phased manner so that temperature at which the fixing ratio obtained by the following expression is equal to or less than 80 percent is determined as fixing temperature.

Fixing ratio (%) = (image density after tape removal/image density before tape attachment) \times 100

[0056]

② Method for evaluating storage stability against heat

The toner is filled in a glass container of 50 cc and placed in a constant temperature bath at 60 °C for 4 hours. Then the toner

is cooled down to the room temperature so that a penetration test (JIS K2235-1991) is conducted for measuring penetration. A high value of the penetration is indicative of a good storage stability against heat.

5 [0057]

③ Method for evaluating an image

An initial image and a copy image after 50000 operations are produced by an IMAGIO 420 manufactured by Ricoh Co. , Ltd., at normal temperature and normal humidity (18 to 27 °C, 30 to 70 %) so that
10 image evaluation is performed by measuring fogging and image density.

The fogging is generally measured based on a following criterion.

A: Very good. No fogging.

B: Good. A little fogging.

15 C: Tolerably good. Fogging arises, but practically not problematic.

D: Poor. Heavily fogging.

The image density is measured with the Macbeth densitometer. Higher image density is indicative of greater coloring strength.

20 [0058]

④ X-ray diffraction measurement

Measurement is performed by means of $\text{CuK}\alpha$ radiation with a RINT1100 manufactured by Hitachi, Ltd.

X-ray tube: Cu, tube voltage: 50 KV, tube current: 30 Ma, scan speed:
25 2 degrees/min.

[0059]

[Method for measuring properties of the black iron oxide compound]

⑤ Average primary particle diameter

The average primary particle diameter is an average of values

obtained by measurements of an electron micrograph by a Hitachi transmission electron microscope H-9000.

[0060]

⑥ Magnetic properties

5. Measurement of the magnetic properties is carried out by using a magnetization measurement device BHU-60 manufactured by Riken Denshi Co., Ltd. Saturation magnetization, residual magnetization, and coercive force are determined from a hysteresis loop obtained by applying a magnetic field swept to 10 kOe to the toner filled
10 in a cell with an inner diameter of 7 mm and a height of 10 mm.

Table 4 shows evaluation results.

[0061]

Embodiments 2 through 6

- The toner is produced in a similar manner to Embodiment 1 except
15 that compounds as shown in Table 2 are used as the black iron oxide compound.

[0062]

Embodiment 2	Embodiment 3	Embodiment 4	Embodiment 5	Embodiment 6
Black iron oxide compound 2	Black iron oxide compound 3	Black iron oxide compound 4	Black iron oxide compound 5	Black iron oxide compound 6

[0063]

Embodiment 7

- 20 (Toner Formula)

Styrene-n-BMA-2EHA copolymer

(T_m 150 °C, T_g 62 °C)

30 parts by weight

Styrene-n-butylacrylate copolymer

(T_m 99 °C, T_g 68 °C)

40 parts by weight

- 25 Black iron oxide compound 7

23 parts by weight

Carnauba wax

5 parts by weight

Charge control agent (chrome azo dye)

2 parts by weight

The materials as described in the formula are kneaded, pulverized, and classified by using the twin screw extruder so that particles of 5 μ m weight average particle diameter are formed. Then silica fine powder (R-972, manufactured by Client Japan) of 1 part by weight is mixed in with the Henschel mixer so as to obtain toner. In the toner formula, "n-BMA" denotes n-butylmethacrylate, and "2EHA" denotes 2-ethylhexylacrylate.

[0064]

Embodiment 8

10 (Toner Formula)

Polyester (Tm 148 °C, Tg 64 °C)	30 parts by weight
Polyester (Tm 100 °C, Tg 60 °C)	40 parts by weight
Black iron oxide compound 8	23 parts by weight
Carnauba wax	5 parts by weight
15 Charge control agent (chrome azo dye)	2 parts by weight

The materials as described in the formula are kneaded, pulverized, and classified by using the twin screw extruder so that particles of 6 μ m weight average particle diameter are formed. Then silica fine powder (R-972, manufactured by Client Japan) of 0.7 parts by weight is mixed in with the Henschel mixer so as to obtain toner.

[0065]

Embodiment 9

(Toner Formula)

Polyester (Tm 152 °C, Tg 60 °C)	35 parts by weight
25 Polyester (Tm 99 °C, Tg 65 °C)	35 parts by weight
Black iron oxide compound 9	25 parts by weight
Carnauba wax	4 parts by weight
Charge control agent (zirconium compound containing 5-methoxy-salicylic acid)	1 part by weight

30 The materials as described in the formula are kneaded, pulverized,

and classified by using the twin screw extruder so that particles of 5.5 μm weight average particle diameter are formed. Then silica fine powder (R-972, manufactured by Client Japan) of 1 part by weight is mixed in with the Henschel mixer so as to obtain toner.

5 [0066]

Comparative examples 1 through 4

The toner is produced in a similar manner to Embodiment 9 except that compounds as shown in Table 3 are used as the black iron oxide compound.

10 [Table 3]

Comparative example 1	Comparative example 2	Comparative example 3	Comparative example 4
Black iron oxide compound 10	Black iron oxide compound 11	Black iron oxide compound 12	Black iron oxide compound 13

[0068]

Evaluations are carried out on the toner of Embodiments 2 through 9 and Comparative examples 1 through 4 in a similar manner to Embodiment 1. Table 4 shows evaluation results.

15 [Table 4]

		X-ray intensity ratio of toner peak A/B	Colorant saturation magnetization (emu/g)	Fixing temperature (°C)	Storage stability against heat (mm)	Fogging after 50000 operations	Image density after 50000 operations
Embodiment	1	0.3	33	160	22	C	1.36
	2	2.0	0.4	160	21	C	1.39
	3	0.3	30	160	23	B	1.42
	4	2.0	0.5	160	23	B	1.39
	5	1.8	28	160	25	A	1.42
	6	0.6	1.8	160	20	A	1.41
	7	1.5	9.5	145	24	A	1.40
	8	1.3	16	130	25	A	1.42
	9	1.0	20	130	30	A	1.41
Comparative example	1	0.9	25	130	28	C	1.11
	2	1.6	10	130	32	D	1.42
	3	0.1	0.9	130	30	D	1.29
	4	2.8	1.2	185	32	C	1.35

[0069]

[Effects of the Invention]

5 The present invention may provide electrostatic image development toner which is excellent in fixability, storage stability against heat, fogging reduction, and image density.

Further, the present invention may provide a method for fixing a toner image formed by using the electrostatic image development toner with high thermal energy efficiency and excellent low
10 temperature fixability.

Furthermore, the present invention may provide a process cartridge including the electrostatic image development toner and an image formation means using the toner.

[Brief Description of the Drawings]

15 [Fig. 1]

Fig. 1 is an illustration showing an example of a fixing device to be used in the present invention.

[Fig. 2]

20 Fig. 2 is a schematic illustration showing an image forming apparatus including a process cartridge of the present invention.

[Reference Numerals]

- 1: Fixing roller
- 2: Pressure roller
- 3: Metal cylinder
- 25 4: Offset prevention layer
- 5: Heat lamp
- 6: Metal cylinder
- 7: Offset prevention layer
- 8: Heat lamp
- 30 T: Toner image
- S: Attachment support member

[Selected Drawing] Fig. 1

[Name of Document] Abstract of the Disclosure

[Abstract]

[Objectives of the Invention]

5 To provide electrostatic image development toner which is
excellent in low temperature fixability, storage stability against
heat, fogging reduction, and image density, a fixing method with
high thermal energy efficiency and excellent low temperature
fixability, a process cartridge including the toner, and an image
formation means using the toner.

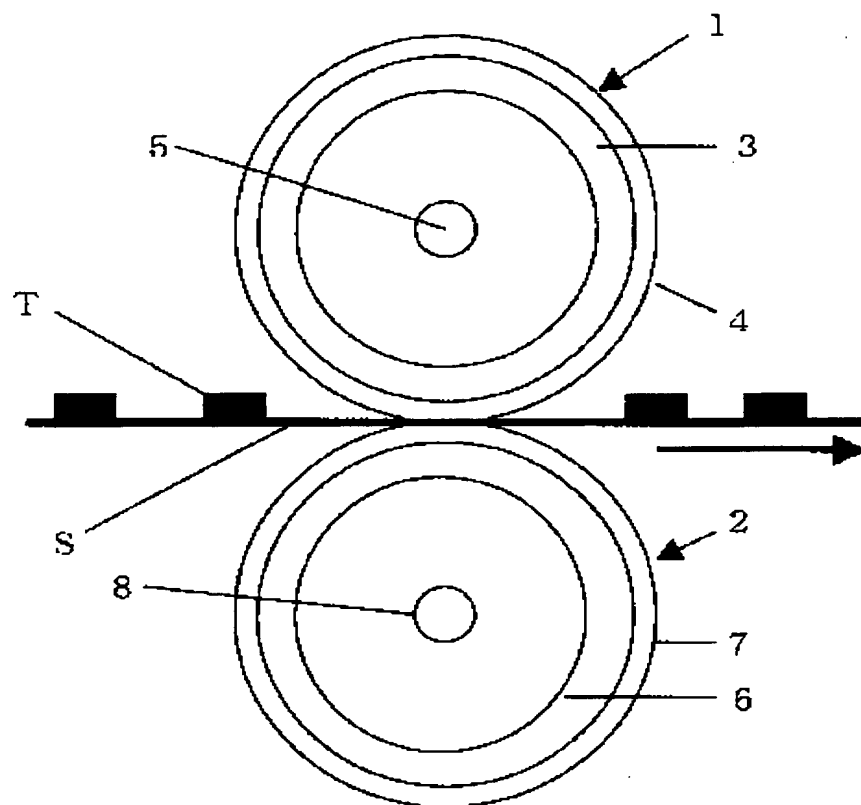
10 [Means for Achieving the Objectives]

Electrostatic image development toner including at least a binder
resin, a charge control agent, and a colorant, characterized in
that the colorant is a black iron oxide compound containing a 10
to 45 weight % titanium component in terms of Ti atoms against Fe
15 atoms in a wavelength dispersive fluorescence spectrometry method,
Bragg angle 2θ peaks of the toner for a $\text{CuK}\alpha$ characteristic X-ray
appear at 32.9 ± 0.3 degrees (peak A) and 35.5 ± 0.3 degrees (peak
B), and an X-ray peak intensity ratio (A/B) for scan speed of 0.5
to 4 degrees/min. is in a range of 0.3 to 2.0.

20

[Name of Document]

[Fig. 1]



[Fig. 2]

